150 ml. of ether. To this solution, 6.6 g. (0.1 mole) of freshly distilled cyclopentadiene was added dropwise. The suspension of white cyclopentadienyllithium was stirred for 15 minutes, and 14.1 g. (0.1 mole) of benzoyl chloride was added dropwise. There was an immediate formation of a bright yellow color. Stirring was continued for 0.5 hr. after the addition was complete, and the reaction mixture was hydrolyzed with dilute aqueous acetic acid. The ether layer was separated and the aqueous layer extracted twice more with ether. After the combined extracts had been dried over Drierite, the solvent was removed by evaporation to leave a brick-red solid. After recrystallization from glacial acetic acid, which removed combined lithium salts, there was obtained 5.1 g. (37%) of orange crystals of the fulvene, m.p. 101–102°. The melting point was raised to 102–103° by recrystallization from hexane; λ_{max}^{EtOH} 264 mμ (log ϵ 4.16), 282 mμ (shoulder) (log ϵ 4.11), 343 mμ (log ϵ 4.01). *Anal.* Calcd. for $C_{19}H_{14}O_2$: C, 83.2; H, 5.15; mol. wt., 274.3. Found: C, 83.5, 83.2; H, 5.3, 5.3; mol. wt., 290.

1,4-Diphenylcyclopent[d]-1,2-oxazine (III).—A solution of 1.0 g. of 1-benzoyl-6-hydroxy-6-phenylfulvene and 1.0 g. of hydroxylamine hydrochloride in 5 ml. of absolute ethanol and 5 ml. of pyridine was refluxed for 2 hr. The solvent was removed by evaporation, and the residual solid was washed with water and recrystallized from absolute ethanol to give 0.73 g. (74%) of orange plates of the oxazine, m.p. 143–143.5°; λ_{max}^{EtOH} 230 mμ (log ϵ 4.29), 244 mμ (log ϵ 4.32), 338 mμ (log ϵ 3.94). *Anal.* Calcd. for $C_{19}H_{13}NO$: C, 84.1; H, 4.8; N, 5.2. Found: C, 84.1; H, 4.9; N, 4.7, 4.8.

1,4-Diphenyl-2-cyclopenta[d]pyridazine (II).—A solution of 1.0 g. of 1-benzoyl-6-hydroxy-6-phenylfulvene and 1.0 g. of 85% hydrazine hydrate in 20 ml. of absolute ethanol was heated under reflux for 2 hr. When the solution was cooled, crystals of the pyridazine separated. There was obtained 0.8 g. (81%) of fluffy yellow crystals, m.p. 205–207°. Recrystallization from absolute ethanol raised the m.p. to 211–212°. *Anal.* Calcd. for $C_{19}H_{14}N_2$: C, 84.4; H, 5.2; N, 10.4. Found: C, 84.6; H, 5.3; N, 10.3, 10.4. The infrared spectrum of the pyridazine exhibited an N–H stretching vibration at 2.97 μ.

Substituted dibenzoylcyclopentadienes were prepared from cyclopentadienyllithium and substituted benzoyl chlorides using procedures similar to that described above.

1-*p*-Toluyl-6-hydroxy-6-*p*-tolylfulvene (IV) was obtained in 44% yield as orange crystals, m.p. 148–149° (from benzene); λ_{max}^{EtOH} 275 mμ (log ϵ 4.23), 348 mμ (log ϵ 4.04). *Anal.* Calcd. for $C_{21}H_{18}O_2$: C, 83.4; H, 6.0. Found: C, 83.6; H, 6.1.

The corresponding oxazine derivative VI melted at 163–165° dec. (from benzene); λ_{max}^{EtOH} 233 mμ (log ϵ 4.26), 341 mμ (log ϵ 4.05). *Anal.* Calcd. for $C_{21}H_{17}NO$: C, 84.2; H, 5.7; N, 4.7. Found: C, 84.5; H, 5.8; N, 4.2.

1-*p*-Chlorobenzoyl-6-hydroxy-6-*p*-chlorophenylfulvene (VII) was obtained in 50% yield, m.p. 175–177° (from a benzene–hexane mixture). *Anal.* Calcd. for $C_{19}H_{12}O_2Cl_2$: C, 66.5; H, 3.5; Cl, 20.7. Found: C, 66.6; H, 3.7; Cl, 20.5.

The oxazine derivative VIII was formed in 62% yield. It melted at 187–188° dec. (from benzene). *Anal.* Calcd. for $C_{19}H_{11}NOCl_2$: C, 67.1; H, 3.3; N, 4.1; Cl, 20.8. Found: C, 67.5; H, 3.3; N, 4.0; Cl, 20.5.

1-*o*-Chlorobenzoyl-6-hydroxy-6-*o*-chlorophenylfulvene (IX) was formed in 26% yield. The yellow crystals were recrystallized from a mixture of ethyl alcohol and ethyl acetate. The melting point showed considerable variation after each recrystallization. The highest observed was 146–147.5°. *Anal.* Calcd. for $C_{19}H_{12}Cl_2O_2$: C, 66.5; H, 3.55; Cl, 20.6. Found: C, 66.7; H, 3.6; Cl, 20.6.

1-*p*-Nitrobenzoyl-6-hydroxy-6-*p*-nitrophenylfulvene (X) was obtained in 39% yield. Recrystallization from dimethylformamide gave yellow, feathery needles, m.p. 248–250°. *Anal.* Calcd. for $C_{19}H_{12}N_2O_6$: C, 62.6; H, 3.3. Found: C, 63.1; H, 3.6. The fulvene also could be recrystallized from dioxane to give brick-red crystals, m.p. 253–255°. *Anal.* Calcd. for $C_{19}H_{12}N_2O_6$: C, 62.6; H, 3.3. Found: C, 62.7; H, 3.5.

Potassium and Sodium Salts of 1-*p*-Chlorobenzoyl-6-hydroxy-6-*p*-chlorophenylfulvene.—A solution of 5 g. of 1-*p*-chlorobenzoyl-6-hydroxy-6-*p*-chlorophenylfulvene in 25 ml. of 20% ethanolic potassium hydroxide was refluxed on the steam-bath for 1 hr. The reaction mixture was cooled and the bright yellow solid separated by filtration. After the yellow crystals had been washed twice with cold ethanol and air-dried, the yellow crystals weighed 5.7 g. The salt was recrystallized twice from benzene–ethyl acetate to give yellow needles that decomposed but did not melt in the range 200–215°. *Anal.* Calcd. for $C_{19}H_{11}O_2K$: C, 59.8; H, 2.9; K, 10.3. Found: C, 59.6; H, 3.3; K, 9.9.

A sample of the potassium salt was dissolved in boiling glacial acetic acid. The crystals which deposited when the solution cooled were collected by filtration and washed with water. The yellow crystals melted at 173–174° after one recrystallization from hexene containing a little benzene. The melting point of a mixture of this material and 1-*p*-chlorobenzoyl-6-hydroxy-6-*p*-chlorophenylfulvene (m.p. 174–176°) was 174–176°.

The sodium salt was prepared in a similar manner except that sodium ethoxide was prepared by dissolving sodium in ethanol. From 1.0 g. of the fulvene there was obtained 0.5 g. of yellow crystals that did not melt or decompose below 250°. Analysis indicated that this salt crystallized with 2 molecules of water. *Anal.* Calcd. for $C_{19}H_{11}O_2Cl_2Na \cdot 2H_2O$: C, 56.9; H, 3.8; Na, 5.7. Found: C, 57.3; H, 3.6; Na, 5.9.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Thermal Condensation of Formaldehyde with Acyclic Olefins[1]

BY A. T. BLOMQUIST, M. PASSER,[2] C. S. SCHOLLENBERGER[2] AND JOSEPH WOLINSKY[2]

RECEIVED MARCH 30, 1957

Thermal condensation of formaldehyde with 1- and 2-heptene, 2-methyl-1-heptene and 2-ethyl-1-butene in solvent acetic acid affords, respectively, the acetates of *trans*-3-octen-1-ol, a mixture of 2-methyl-3-hepten-1-ol (70%) and 2-vinyl-1-hexanol (30%), 3-methylene-1-octanol and 3-ethyl-3-penten-1-ol. These observations are in agreement with the postulation that reaction proceeds *via* a planar six-membered ring transition state.

The behavior of a representative group of acyclic olefins in the thermal condensation with formaldehyde has been studied with the object of establishing the scope and limitations of the reaction as a useful synthetic method for unsaturated primary alcohols and related compounds. Another objective was to obtain additional knowledge pertinent to the operating mechanism.

Various workers have shown that the principal

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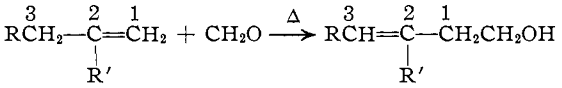
[1] The work reported here was done as part of a general research program in organic chemistry at Cornell University sponsored by The B. F. Goodrich Co.

[2] Abstracted from part of the dissertations presented by M. Passer in September, 1948, C. S. Schollenberger in September, 1947, and J. Wolinsky in June, 1956, to the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

products of thermal olefin–formaldehyde condensations are unsaturated primary alcohols in which the double bond is located at a position adjacent to its original site in the starting olefin.[3] The only known exception to this is camphene, which is reported to give an "allylic" type alcohol.[3b]



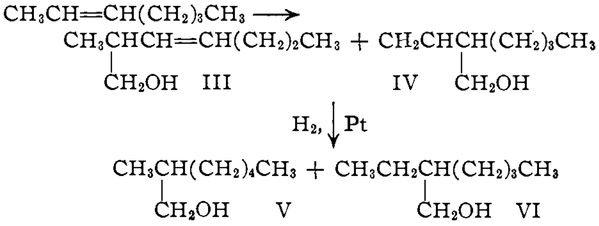
$$\mathrm{R\overset{3}{C}H_2{-}\underset{R'}{\overset{2}{C}}{=}\overset{1}{C}H_2 + CH_2O \xrightarrow{\Delta} R\overset{3}{C}H{=}\underset{R'}{\overset{2}{C}}{-}\overset{1}{C}H_2CH_2OH}$$

In this study all condensations were carried out in solvent acetic acid or acetic anhydride–acetic acid at temperatures varying from 130 to 195°, products being obtained as acetates.[4]

From the condensation of 1-heptene (at 180°) *trans*-3-octen-1-ol acetate (I) was obtained in *ca.* 20% yield.[5] The infrared absorption spectrum of this I indicated that it always contained some of the corresponding formate. Hydrolysis of this I afforded *trans*-3-octen-1-ol (II) from which pure I was obtained by acetylation. The structure of I was established by (1) reduction and hydrolysis to 1-octanol and (2) by reductive ozonolysis to *n*-valeraldehyde. Further, oxidative ozonolysis of II gave *n*-valeric acid. Both I and II showed strong absorption in the infrared at 10.35 μ indicating that they possessed the *trans* configuration. This was confirmed by independent synthesis of *cis*- and *trans*-II from 3-octyn-1-ol. The *trans*-II thus obtained was identical in all respects with II obtained in the 1-heptene–formaldehyde condensation.

That *cis*-I is not an intermediate in the reaction was indicated by the observation that only *cis*-I was recovered when pure *cis*-II was heated at 170° for 20 hr. with formaldehyde in solvent acetic acid–acetic anhydride.

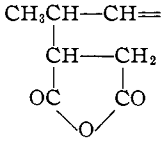
Condensation of formaldehyde with 2-heptene under conditions similar to those used for 1-heptene gave, after *trans*-esterification, a mixture of two unsaturated alcohols III and IV in *ca.* 20% yield. This product, which showed a very narrow b.p. range, gave no solid derivatives and its direct separation into the two isomeric components was not attempted. Reduction of the mixture of alcohols III and IV gave a product comprising 70% 2-methyl-1-heptanol (V) and 30% 2-ethyl-1-hexanol (VI). This composition was established by comparing the infrared absorption spectrum of the reduction product with spectra of known mixtures of pure V and VI obtained independently. Solid crystalline derivatives could be obtained from the mixture of V and VI, the 3,5-dinitrobenzoate of V and the α-naphthylurethan derivative of VI.[6]



$$\mathrm{CH_3CH{=}CH(CH_2)_3CH_3 \longrightarrow \underset{III}{CH_3\underset{CH_2OH}{C}HCH{=}CH(CH_2)_2CH_3} + \underset{IV}{CH_2C\underset{CH_2OH}{H}CH(CH_2)_3CH_3}}$$

$$\Big\downarrow \mathrm{H_2, Pt}$$

$$\mathrm{\underset{V}{CH_3\underset{CH_2OH}{C}H(CH_2)_4CH_3} + \underset{VI}{CH_3CH_2\underset{CH_2OH}{C}H(CH_2)_3CH_3}}$$



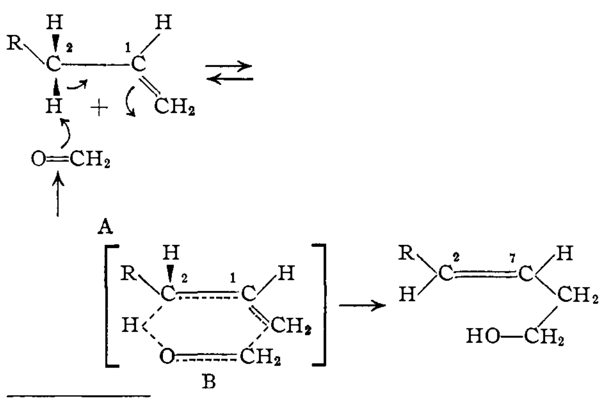
VII

From the condensation of 2-methyl-1-heptene (at 130–140°) 3-methylene-1-octanol acetate (VIII) containing some 3-methyl-3-octen-1-ol acetate (IX) was obtained in *ca.* 30% yield. Hydrolysis of this product followed by reduction gave 3-methyl-1-octanol (X). Ozonolysis of the original reaction product gave formaldehyde as its methone derivative in 54% yield indicating that VIII was its principal constituent. This was confirmed by noting that the hydrolyzed reaction product, unsaturated alcohols, showed strong infrared absorption at 11.25 μ and gave only a low yield (*ca.* 7%) of *n*-valeric acid on ozonolysis.

Finally, from the condensation of 2-ethyl-1-butene (at 160–165°) there was obtained 3-ethyl-3-penten-1-ol acetate (XI) in *ca.* 45% yield. Ozonolysis of the alcohol obtained by hydrolysis of XI gave acetaldehyde while reduction of this alcohol afforded 3-ethyl-1-pentanol. Oxidation of the latter gave the known 3-ethylpentanoic acid.

The foregoing observations indicate that the thermal condensation of formaldehyde with acyclic olefins occurs most readily with isobutylene type olefins, $\mathrm{CH_2{=}CR_2}$, and that monosubstituted and disubstituted olefins of the type $\mathrm{CH_2{=}CHR}$ and $\mathrm{RCH{=}CHR'}$ are markedly less reactive. Further, the observations are in reasonable accord with the commonly accepted mechanism for the condensation which postulates the intermediate formation of a six-membered ring cyclic transition state.[3f]

Thus the formation of exclusively *trans*-3-octen-1-ol from 1-heptene is to be expected from a consideration of the model



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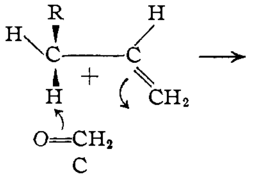
(3) (a) O. Kriewitz, *Ber.*, **32**, 57 (1899); (b) G. Langlois, *Ann. chim.* (*Paris*), **12**, 290 (1919); (c) H. J. Prins, *Chem. Weekblad*, **16**, 1510 (1919). *C. A.*, **14**, 1119 (1920); (d) J. J. Ritter, U. S. Patent 2,335,027 *C. A.*, **38**, 2662 (1944); (e) J. P. Bain, THIS JOURNAL, **68**, 638 (1946); (f) R. T. Arnold and J. F. Dowdall, *ibid.*, **70**, 2590 (1948); (g) R. T. Arnold, R. W. Amidon and R. M. Dodson, *ibid.*, **72**, 2871 (1950); (h) B. N. Rutovskii and L. A. Alferova, *C. A.*, **46**, 7545 (1952); (i) A. T. Blomquist, British Patent 657,497, *C. A.*, **46**, 11231 (1952); (j) G. Ohloff, *Arch. Pharm.*, **287**, 258 (1954); (k) A. T. Blomquist and J. A. Verdol., THIS JOURNAL, **77**, 78 (1955); (l) N. O. Brace, *ibid.*, **77**, 4666 (1955).

(4) Since a substantial amount of the formaldehyde disproportionates, under the reaction conditions, to methanol and formic acid, there seems to be no real distinction between condensations carried out with and without acetic acid. Previous experience has shown, however, that use of solvent acetic acid improves the yield (see ref. 3k).

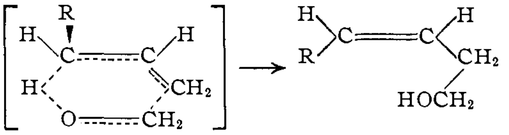
(5) Brace reported the formation of *trans*-3-nonadecen-1-ol in the thermal condensation of 1-octadecene with formaldehyde (see ref. 3l).

(6) It is of interest here to note that the closely related condensation of maleic anhydride with 2-pentene affords but a single product, the anhydride VII; K. Alder and H. Söll, *Ann.*, **565**, 57 (1949).

With the olefin in an extended staggered conformation such as A two equivalent paths of approach are available to the formaldehyde molecule to form the cyclic transition state B having hydrogen atoms disposed in *trans* arrangement at carbon atoms 1 and 2. From B only a *trans*-olefinic alcohol can result. The formation of a *cis*-product would, by this mechanism, require that the reacting olefin be in a higher energy folded conformation such as C.[7] Examination of molecular models gives a clearer picture of the above.



C



D

The favored formation of 2-methyl-3-hepten-1-ol over 2-vinyl-1-hexanol from 2-heptene is possibly due to (1) a sterically favored path to the requisite transition state and (2) the lower energy requirements for the formation of the disubstituted olefin. In condensations of isobutylene-type olefins such as $RC(CH_3){=}CH_2$, *e.g.*, 2-methyl-1-heptene, predominant formation of 3-methylene-1-alkanols is probably a consequence of the more acidic nature of the methyl hydrogens[8] favoring the formation of the requisite transition state.[9]

Experimental Part[10]

Materials.—1-Heptene, b.p. 91–93° (749 mm.), n^{20}D 1.4016, was prepared in 68% yield by the reaction of *n*-butylmagnesium bromide with allyl bromide.[11] Research grade 2-heptene was obtained from the Phillips Petroleum Co. and 2-ethyl-1-butene, min. purity 95%, from the Connecticut Hard Rubber Co. 2-Methyl-1-heptene, b.p. 115–118°, was prepared in 61% yield by the method of Tamele, *et al.*[12]

Condensation of 1-Heptene with Formaldehyde.—A mixture of 76.4 g. (0.78 mole) of 1-heptene, 24.6 g. (0.78 mole) of paraformaldehyde and 46.8 g. (0.78 mole) of glacial acetic acid was heated in a Pyrex bomb at 185–190°, with agitation, for 60 hours. The reaction mixture was distilled free of water and unreacted starting materials. The combined residues of two experiments were refluxed with acetic anhydride and pyridine. Most of the pyridine and excess acetic anhydride were then removed by distillation at 100 mm. and the residue washed with water, aqueous sodium carbonate and water. After drying, the reaction product was distilled to give the following fractions: (a) 2.04 g. of forerun, b.p. 23–88.5°; (b) 45.72 g. of I, b.p. 88.5–98°, n^{20}D 1.4335–1.4330; (c) 12.45 g. of mainly I, b.p. 97–117°, n^{20}D 1.4347; and (d) 7.23 g. of higher condensation products, b.p. 117–131°, n^{20}D 1.4483. The still residue was 11.6 g. The over-all yield, based on 1-heptene charged, of redistilled I, b.p. 92–95° (17 mm.), n^{25}D 1.4308, d^{25}_{4} 0.8845, was 17%.

The infrared spectrum of the compound I described above showed strong absorption at 8.55 μ (formate ester) and at 5.75 and 8.05 μ (acetate). Pure I, uncontaminated with formate, was obtained by acetylating pure II and showed b.p. 90–92° (13 mm.), n^{25}D 1.4307, d^{25}_{4} 0.8862 (Normant reported[13] b.p. 93° (12 mm.), d^{13}_{16} 0.893).

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66; *MR*D, 49.6. Found: C, 70.18; H, 10.73; *MR*D, 49.7.

Quantitative hydrogenation of I in ethanol using Adams catalyst required 99% of one molar equivalent of hydrogen. From 25 g. of I there was obtained 16.7 g. of a colorless liquid, b.p. 198–203°, n^{20}D 1.4229 (reported for 1-octanol acetate, b.p. 210° (760 mm.), d^{20}_{4} 0.885[14]; b.p. 78° (5 mm.), n^{25}D 1.4188).[15] Saponification of this product gave 1-octanol, b.p. 188–192°, n^{20}D 1.4318 (reported b.p. 195°, n^{25}D 1.4275,[16] n^{25}D 1.4298[15]), characterized as its α-naphthylurethan, m.p. 66–67°, and as its phenylurethan, m.p. 73–74°. The m.p.'s of these derivatives were not depressed when mixed with the corresponding derivatives of authentic 1-octanol.

Reductive ozonolysis of 9.5 g. of I gave 1.1 g. of distilled liquid product 0.3 g. of which showed b.p. 112–120°, n^{20}D 1.4091 (reported[17] for *n*-valeraldehyde, b.p. 103.7°, n^{20}D 1.3944). The 2,4-dinitrophenylhydrazone derivative of this product showed m.p. 104.5–105.5° and did not depress the m.p. of authentic *n*-valeraldehyde 2,4-dinitrophenylhydrazone having m.p. 106.5–107.5°. It did depress the m.p. of authentic *n*-hexaldehyde 2,4-dinitrophenylhydrazone having m.p. 104.7–105.7°. No other product was isolated from the ozonolysis.

cis-II.—In a Parr apparatus 14.8 g. (0.117 mole) of 3-octyn-1-ol (Farchan) in methanol was reduced at room temperature using 1.5 g. of Lindlar catalyst.[18] Absorption of 0.117 mole of hydrogen was complete in 5 hours. Distillation of the filtered hydrogenation mixture gave 12.3 g. (83%) of *cis*-II. A center cut showed b.p. 96° (25 mm.), n^{25}D 1.4450, d^{25}_{4} 0.8464, and no maximum in the infrared at 10.35 μ (*trans*-RCH=CHR).

Anal. Calcd. for $C_8H_{16}O$: C, 74.94; H, 12.58; *MR*D, 40.27. Found: C, 75.08; H, 12.37; *MR*D, 40.31.

The α-naphthylurethan derivative, after three recrystallizations from pentane, showed m.p. 28–29.5°.

Anal. Calcd. for $C_{19}H_{23}O_2N$: C, 76.73; H, 7.80. Found: C, 76.96; H, 7.83.

The 3,5-dinitrobenzoate derivative, after recrystallization from ethanol, showed m.p. 38.5–39.5°. This derivative oiled when mixed with the 3,5-dinitrobenzoate of *trans*-II.

Anal. Calcd. for $C_{15}H_{18}O_6N_2$: C, 55.89; H, 5.63. Found: C, 56.36; H, 5.49.

cis-I.—A mixture of 7.0 g. of *cis*-II, 6 ml. of acetic acid, 5 ml. of acetic anhydride and 0.3 g. of paraformaldehyde was heated at 170–175° in a sealed Pyrex tube for 20 hours. From the reaction mixture there was obtained 8.64 g. of *cis*-I, b.p. 105–108° (25 mm.), n^{25}D 1.4317, d^{25}_{4} 0.8898. The infrared spectrum of this acetate showed no absorption at 3.0 μ (hydroxyl group) and very slight absorption at 10.28 μ indicating the possible presence of only a trace of the *trans*-acetate.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.65; *MR*D, 49.60. Found: C, 71.20; H, 10.71; *MR*D, 49.60.

trans-II.[19]—A solution of 22 g. (0.174 mole) of 3-octyn-1-ol (Farchan) was added slowly to a solution of 25 g. (1.09 gram atoms) of sodium in 1 l. of liquid ammonia. After stirring the mixture for 3 hours, 60 g. of ammonium chloride was added cautiously over a 2-hour period. The ammonia

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[7] M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., p. 7.

[8] Reference 7, p. 439.

[9] Although the above rationalizations appear to account fairly satisfactorily for the observed behavior of acylic olefins in their thermal condensation with formaldehyde, the presence of formic acid in the reaction medium makes it difficult to exclude completely the possible operation of acid-catalyzed mechanisms.

[10] All melting points and boiling points are uncorrected. Infrared spectra were determined using a Perkin-Elmer double beam infrared spectrophotometer, model 21.

[11] A. Kirrman, *Bull. soc. chim. France*, [4] **39**, 990 (1926).

[12] M. Tamele, C. J. Ott, K. E. Marple and G. Hearne, *Ind. Eng. Chem.*, **33**, 120 (1941).

[13] H. Normant, *Compt. rend.*, **226**, 733 (1948).

[14] R. Gartenmeister, *Ann.*, **233**, 262 (1886).

[15] E. L. Jenner and R. S. Schreiber, This Journal, **73**, 4351 (1951).

[16] G. L. Dorough, H. B. Glass, T. L. Gresham, G. B. Malone and E. E. Reid, *ibid.*, **63**, 3100 (1941).

[17] I. Simon, *Bull. soc. chim. Belg.*, **38**, 56 (1929).

[18] H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

[19] Crombie and S. H. Harper, *J. Chem. Soc.*, 873 (1950); F. Sondheimer, *ibid.*, 877 (1950).

was evaporated and distillation of the water-washed ether solution of the residue gave 17.6 g. (80%) of colorless *trans*-II, b.p. 101–102° (30 mm.), n^{25}_{D} 1.4432, d^{25}_4 0.8420.

Anal. Calcd. for $C_8H_{16}O$: C, 74.94; H, 12.58; MR_{D}, 40.27. Found: C, 74.96; H, 12.35; MR_{D}, 40.39.

The α-naphthylurethan derivative after recrystallization from 90–100° petroleum ether showed m.p. 70–70.5°.

Anal. Calcd. for $C_{19}H_{23}O_2N$: N, 4.71. Found: N, 4.88, 4.93.

The 3,5-dinitrobenzoate derivative melted at 39–39.4° after recrystallization from ethanol.

Anal. Calcd. for $C_{15}H_{18}O_8N_2$: C, 55.89; H, 5.63; N, 8.69. Found: C, 55.84, 55.71; H, 5.66, 5.51; N, 8.59, 8.59.

The *trans*-II obtained by the saponification of I isolated from the 1-heptane–formaldehyde reaction showed b.p. 82–84° (12 mm.), n^{25}_{D} 1.4429, d^{25}_4 0.8435 (reported[13] for II, b.p. 86° (12 mm.), d^{10}_{16} 0.849).

Anal. Calcd. for $C_8H_{18}O$: C, 74.95; H, 12.58; mol. wt., 128, MR_{D}, 40.27. Found: C, 74.45, 74.59; H, 12.46, 12.59; mol. wt. (cryoscopic in benzene), 128; MR_{D}, 40.29.

The 3,5-dinitrobenzoate, m.p. 39–39.4°, and α-naphthylurethan, m.p. 70–70.5°, derivatives of this *trans*-II did not depress the m.p.'s of like derivatives of authentic *trans*-II.

Oxidative ozonolysis of 5.0 g. of *trans*-II (from I) afforded 0.5 g. of a liquid having b.p. 172–180°, n^{20}_{D} 1.4071 (reported[20] for *n*-valeric acid, b.p. 186° (760 mm.), n^{18}_{D} 1.4099). The *p*-bromophenacyl ester of this product showed m.p. 62.5–63.5° and did not depress the m.p. of authentic *p*-bromophenacyl *n*-valerate, m.p. 63.5–64°. No other cleavage fragment was isolated from the ozonolysis.

Condensation of 2-Heptene with Formaldehyde.—A mixture of 200 g. (2.04 moles) of 2-heptene, 55 g. (1.83 moles) of paraformaldehyde, 96 g. (1.60 moles) of glacial acetic acid and 18.4 g. (0.20 mole) of acetic anhydride was heated in a stainless steel bomb at 180–190°, with agitation, for 40 hours. The reaction mixture was filtered and separated from 24 g. of an aqueous layer. The organic layer was distilled to remove 182.5 g. of starting materials which contained 138.5 g. of unreacted 2-heptene. Continued distillation gave 62.3 g. (60% yield based on 2-heptene consumed) of crude acetate, b.p. 98–107° (30 mm.). The infrared spectrum of this crude acetate showed strong absorption at 5.75 and 8.05 μ (acetate), 8.55 μ (formate), 10.35 μ (*trans*-RCH=CHR), and 10.05 and 10.95 μ (RCH=CH_2).

Transesterification of the entire crude acetate with methanol and dibutyltin oxide catalyst gave 40.2 g. of a colorless liquid (III and IV), b.p. 94–96° (40 mm.), n^{25}_{D} 1.4402, d^{25}_4 0.8467. The infrared spectrum of this product indicated it to be free of acetate and formate. Strong absorption in the infrared at 3.0, 10.35, 10.05 and 10.95 μ indicated the presence of the hydroxyl group, the *trans*-olefinic link, and a terminal double bond.

Anal. Calcd. for $C_8H_{18}O$: C, 74.94; H, 12.58. Found: C, 74.37, 74.15; H, 12.42, 12.24.

The 3,5-dinitrobenzoate and α-naphthylurethan derivatives were liquids.

Hydrogenation of Mixed III and IV.—Upon hydrogenation of 15 g. (0.117 mole) of the mixture of unsaturated alcohols III and IV in ethyl acetate at room temperature using Adams catalyst, one molecular equivalent of hydrogen was absorbed. The reduced product was carefully distilled through a Todd column (50 theoretical plates) and eight fractions were taken over the b.p. range 184–186°. All showed n^{25}_{D} 1.4280.

Anal. Calcd. for $C_8H_{18}O$: C, 73.78; H, 13.93. Found: C, 73.72, 73.69; H, 13.70, 13.89.

A redistilled sample of authentic (±)-VI showed b.p. 96–98° (25–30 mm.), n^{25}_{D} 1.4300 (reported[21] for (±)-VI, b.p. 181–183°, n^{20}_{D} 1.4328). An authentic sample of (±)-V showed b.p. 178.5–182°, 95–97° (35 mm.), n^{25}_{D} 1.4257–1.4258 (reported: (±)-V, b.p. 175.4°, n^{25}_{D} 1.4219[16]; (−)-V, b.p. 85–89° (18 mm.), n^{25}_{D} 1.4256[22]).

The infrared spectrum of the mixture of reduced alcohols V and VI showed no absorption maxima characteristic of 1-octanol. All maxima observed could be accounted for in the combined spectra of V and VI. From a comparison of the infrared spectrum of the mixture with the spectra of known mixtures of V and VI it was estimated that the mixture comprised 70% V and 30% VI.

From 2 g. of the mixture of V and VI there was obtained 2.66 g. of a crystalline 3,5-dinitrobenzoate derivative having m.p. 44–46° which did not depress the m.p. of authentic V 3,5-dinitrobenzoate of m.p. 45–46°. The 3,5-dinitrobenzoate of VI is liquid at room temperature.

From treatment of the mixed alcohols (V and VI) with α-naphthyl isocyanate there was obtained, after many recrystallizations from pentane, a white crystalline α-naphthylurethan derivative, m.p. 52–55°, which did not depress the m.p. of an authentic sample of the α-naphthylurethan derivative of VI, m.p. 55–56°. The α-naphthylurethan derivative of V is liquid at room temperature.

Condensation of 2-Methyl-1-heptene with Formaldehyde.—A mixture of 54.4 g. (0.48 mole) of 2-methyl-1-heptene, 15.3 g. (0.48 mole) of paraformaldehyde, 19.4 g. (0.32 mole) of glacial acetic acid and 16.5 g. (0.16 mole) of acetic anhydride was heated, with agitation, in a Pyrex bomb at 130–140° for 24 hr. Fractional distillation of the light brown product gave 50 g. of a mixture of starting materials and 24.7 g. (29%) of crude VIII, b.p. 62–75° (1–2 mm.). From a 27.1-g. sample of crude VIII after refluxing with acetic anhydride and pyridine there was obtained 16 g. of VIII (plus some IX), of which a center cut showed b.p. 50.2–50.6° (0.3 mm.), n^{20}_{D} 1.4418, d^{20}_4 0.8993.

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94; sapn. no., 184; MR_{D}, 54.2. Found: C, 72.00, 71.72; H, 11.25, 11.22; sapn. no., 187, 184; MR_{D}, 54.2.

Reductive ozonolysis of 0.437 g. of the acetate VIII (containing some IX) afforded 0.372 g. (54%) of methone derivative of formaldehyde, m.p. 186–187°, which did not depress the m.p. of an authentic sample of the derivative.

Saponification of 45.4 g. of the above acetate (VIII + some IX) gave 25.8 g. of unsaturated alcohols predominantly 3-methylene-1-octanol b.p. 63.2–63.4° (1.2 mm.), n^{20}_{D} 1.4533, d^{20}_4 0.8630.

Anal. Calcd. for $C_9H_{18}O$: C, 76.00; H, 12.75; MR_{D}, 44.8. Found: C, 75.42, 75.72; H, 12.51, 13.00; MR_{D}, 44.6.

Oxidative ozonolysis of 12.9 g. of 3-methylene-1-octanol gave 0.6 g. (b.p. 184–185° micro) of a colorless liquid. A portion of this material gave a *p*-bromophenacyl ester, m.p. 71.3–72.6°, which was undepressed by an authentic sample of the phenacyl ester of *n*-valeric acid.

Hydrogenation of 10.9 g. (0.077 mole) of VIII (plus some IX) in ethanol at room temperature using Adams catalyst gave 7.86 g. of X, b.p. 109–109.8° (22 mm.), n^{20}_{D} 1.4325, d^{20}_4 0.8359 (reported for (−)X, b.p. 110° (25 mm.), n^{25}_{D} 1.4328, d^{25}_4 0.827[23]; (±)-X, b.p. 108° (22 mm.), n^{19}_{D} 1.4350.[24]

Anal. Calcd. for $C_9H_{20}O$: C, 74.93; H, 13.98; MR_{D}, 45.40. Found: C, 75.03, 75.13; H, 14.25, 14.30; MR_{D}, 44.80.

Condensation of 2-Ethyl-1-butene with Formaldehyde.—A mixture of 63.1 g. (0.75 mole) of 2-ethyl-1-butene, 23.7 g. (0.75 mole) of paraformaldehyde, 30.0 g. (0.5 mole) of glacial acetic and 25.5 g. (0.25 mole) of acetic anhydride was shaken at 160–165° for 24 hours. On distillation there was obtained 31.5 g. of unreacted olefin and 52.2 g. (44%) of crude XI, b.p. 82–83° (20 mm.), n^{20}_{D} 1.4361, d^{20}_4 0.9101.

Anal. Calcd. for $C_9H_{15}O_2$: C, 69.19; H, 10.33; MR_{D}, 45.0; sapn. no., 156. Found: C, 69.25, 69.30; H, 11.00, 10.73; MR_{D}, 44.9; sapn. no., 154, 153.

Saponification of the above acetate gave 3-ethyl-3-penten-1-ol, b.p. 77.5–78.3° (20 mm.), n^{20}_{D} 1.4505, d^{20}_4 0.8823.

Anal. Calcd. for $C_7H_{14}O$: C, 73.63; H, 12.36; MR_{D}, 35.6. Found: C, 73.92, 73.75; H, 13.00, 12.84; MR_{D}, 34.8.

Reductive ozonolysis of 33 g. of the alcohol gave *ca.* 8 ml. of acetaldehyde identified as its 2,4-dinitrophenylhydrazone derivative, m.p. 165–166.5°, and its methone derivative, m.p. 138.5–140.5°.

Hydrogenation of 10 g. (0.087 mole) of the alcohol in

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(22) P. A. Levene and M. Kuna, *ibid.*, **140**, 255 (1941).

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ethyl ether at room temperature using Adams catalyst gave 8.8 g. of 3-ethyl-1-pentanol, b.p. 90–91.5° (30 mm.), n^{20}_D 1.4287, d^{20}_4 0.8398.

Anal. Calcd. for $C_7H_{16}O$: C, 72.35; H, 13.88; MR_D, 36.1. Found: C, 72.03, 72.37; H, 14.10, 14.20; MR_D, 35.6.

Oxidation of 2.8 g. of 3-ethyl-1-pentanol by the method of Fournier[25] gave 1.04 g. of 3-ethyl-1-pentanoic acid, b.p. 207–208.5° (reported[26] for 3-ethyl-1-pentanoic acid, b.p. 212°. The amide was obtained as flaky plates from ethanol; m.p. 128.5–129.5° (reported[27] m.p. 127.5°). The piperazonium salt prepared by the method of Pollard[28] showed m.p. 133–134° (reported[29] m.p. 133–134°).

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ITHACA, N. Y.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Thermal Condensation of Cyclic Olefins with Formaldehyde[1,2]

BY A. T. BLOMQUIST, JOSEPH VERDOL,[3] CLAIRE L. ADAMI, JOSEPH WOLINSKY[3] AND DONALD D. PHILLIPS

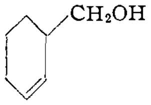
RECEIVED MARCH 30, 1957

Thermal condensation of formaldehyde with cyclohexene, *pure* α-pinene, *d*-limonene and 1-methylcyclohexene either in the presence of solvent acetic acid–acetic anhydride or in the absence of solvent affords, respectively, as principal products 2-cyclohexenemethanol acetate, 2-methylene-6,6-dimethylbicyclo[3.3.1]heptane-3-methanol, "homolimonenol," and an approximately equal mixture of 2-acetoxymethylmethylenecyclohexane and 3-acetoxymethyl-2-methylcyclohexene. The formation of these products is in accord with a postulation that suggests a planar six-membered ring for the transition state of the reaction.

A recent article presented our observations on the behavior of representative acyclic olefins in their thermal condensation with formaldehyde.[2] It seemed desirable to extend this study by examining also the thermal condensation of some typical cyclic olefins with formaldehyde. There was special interest in the behavior of α-pinene, *d*-limonene and cyclohexene as these olefins have been reported to be essentially unreactive in the condensation.[4–6] On the basis of our earlier work with the acyclic olefins[2] such cyclic olefins would be expected to be reactive albeit to perhaps a lesser extent. We have found, in fact, that the olefins cyclohexene, 1-methylcyclohexene, α-pinene and *d*-limonene do react with formaldehyde to afford monocondensation products to the extent of 10–54%.

The condensations with paraformaldehyde were carried out either in the presence or absence of solvent acetic acid–acetic anhydride at temperatures varying from 160–180°. The principal products obtained were primary unsaturated alcohols or their acetates in which the double bond occupied a position adjacent to that in the starting cyclic olefin.

The condensation of cyclohexene at 180° in solvent acetic acid–acetic anhydride gave the crude acetate of 2-cyclohexenemethanol (I) in *ca.* 10% yield together with a small amount of higher boiling material.[7] Although I has not been described previously all of its pertinent isomers have been reported. The properties of I and three of its crystalline derivatives did not correspond to those reported for 1-cyclohexenemethanol,[8] 4-cyclohexenemethanol,[9,10] 2-methylenecyclohexanol[8,11,12] and 2-methyl-1-cyclohexene-3-ol.[13,14] A tetrahydrobenzyl alcohol whose phenylurethan derivative showed m.p. 63°, was reported by Pommereau.[15] This may have been I as the phenylurethan derivative of our I showed m.p. 61–63°. The infrared absorption spectrum of I showed maxima at 13.83, 14.40 and 14.80 μ which are observed for 3-methyl and 4-methyl-1-cyclohexene, etc.,[16] and appear to be characteristic of an unsubstituted carbocyclic



I; Ia, the acetate

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[1] The work reported here was done as part of a general research program in organic chemistry at Cornell University sponsored by the B. F. Goodrich Co.

[2] For a closely related preceding paper see A. T. Blomquist, M. Passer, C. S. Schollenberger and Joseph Wolinsky, THIS JOURNAL, **79**, 4972 (1957).

[3] Abstracted from part of the dissertations presented by J. Verdol in February, 1955, and J. Wolinsky in June, 1956, to the Graduate School of Cornell University in partial fulfillment of the requirements for the Degree Doctor of Philosophy. Part of the work reported here was done by Miss Claire Adami in conjunction with the Honors Program in Chemistry.

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[6] N. O. Brace reported that cyclohexene and α-pinene do react with paraformaldehyde at 200–225° but gave no information about yield or structure of the products (THIS JOURNAL, **77**, 4666 (1955)).

[7] The mixture contained *trans*-2-hydroxymethyl-1-cyclohexanol diacetate (II) and possibly the diacetates of 1,3-bis-(hydroxymethyl)-cyclohexene (III) and 3,4-bis-(hydroxymethyl)-cyclohexene (IV). Evidence for II was the isolation of its bisphenylurethan derivative. The possible presence of III and/or IV was suggested by the observation that the mixture absorbed 75% of one equivalent of hydrogen upon catalytic reduction.

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[15] H. Pommereau, *Compt. rend.*, **174**, 685 (1922).

[16] "Catalogue of Selected Infrared Absorption Spectrograms." American Petroleum Institute Research, Project 44, National Bureau of Standards, Washington, D. C.